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Synthesis and superstructural characterization of $Fe_{1.89}Mo_{4.11}O_7$

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Abstract
Superstructuring in the new compound $Fe_{1.89}Mo_{4.11}O_7$ has been elucidated by transmission electron microscopy. This compound is a member of the family $M_2MO_4O_7$ and has both iron and molybdenum atoms occupying octahedrally coordinated sites in the structure, represented by $Fe^t(Fe_{0.89}M_{0.11})^0Mo_4O_7$. The superstructuring, detected only by electron diffraction, involved tripling of all three lattice parameters of the subcell. The subcell was structured by single crystal x-ray diffraction [Imma, no. 74, a = 5.9793(5) Å, b = 5.7704(4) Å, and c = 17.036(1) Å]. This structure type contains a close-packed arrangement of Mo_4O_7 units, which are infinite chains of trans edge-shared molybdenum octahedra running parallel to b*. Two different coordination environments are observed for the cations. Parallel to the a* direction, infinite edge-sharing MO_6 (M = 89% Fe or 11% Mo) octahedra are observed. The second cation site, with nearly tetrahedral coordination by oxygen, is filled solely by iron. The superstructure can be rationalized by a regular arrangement of iron and molybdenum atoms in the octahedrally coordinated cation sites.

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Synthesis and superstructural characterization of $Fe_{1.89}Mo_{4.11}O_7$

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Superstructuring in the new compound $Fe_{1.89}Mo_{4.11}O_7$ has been elucidated by transmission electron microscopy. This compound is a member of the family $M_2Mo_4O_7$ and has both iron and molybdenum atoms occupying octahedrally coordinated sites in the structure, represented by $Fe^t(Fe_{0.89}Mo_{0.11})^oMo_4O_7$. The superstructuring, detected only by electron diffraction, involved tripling of all three lattice parameters of the subcell. The subcell was structured by single crystal x-ray diffraction [*Imma*, no. 74, $a = 5.9793(5)$ Å, $b = 5.7704(4)$ Å, and $c = 17.036(1)$ Å]. This structure type contains a close-packed arrangement of Mo_4O_7 units, which are infinite chains of trans edge-shared molybdenum octahedra running parallel to b^*. Two different coordination environments are observed for the cations. Parallel to the a^* direction, infinite edge-sharing MO_6 (M = 89% Fe or 11% Mo) octahedra are observed. The second cation site, with nearly tetrahedral coordination by oxygen, is filled solely by iron. The superstructure can be rationalized by a regular arrangement of iron and molybdenum atoms in the octahedrally coordinated cation sites.

I. INTRODUCTION

The $FeMo_2S_4$[1] phase contains a spinel-related structure in which distortions occur to form irregular chains of molybdenum with diamond-shaped Mo_4 cluster units. This ternary molybdenum sulfide contains Mo–Mo bonded units due to a multidirectional Peierls distortion. However, the analogous oxide, $FeMo_2O_4$, is not known, even though metal-metal bonding in molybdenum oxide systems is quite common.[2–6] The compound to be discussed, $Fe_{1.89}Mo_{4.11}O_7$, was formed as the principal product in a reaction which was intended to prepare $FeMo_2O_4$.

The structural characterization of such a new material is essential for understanding its properties. In the investigation of novel materials, the elucidation of structural details can provide valuable insight into why the formation of certain compounds is promoted and other phases are not. However, the structural characterization of new materials becomes increasingly more difficult when atomic sites are occupied by more than one type of cation and/or where variable cation populations cause distortions in the basic framework. $Fe_{1.89}Mo_{4.11}O_7$ is one such material. It not only possesses mixed metal sites and structural framework distortions, but also contains a stacking arrangement of the infinite chains composed of trans edge-shared molybdenum octahedra not previously observed. To date, these infinite chains of molybdenum octahedra have been found to interconnect, or stack, in five different manners. These structure types are exemplified in $NaMo_4O_6$,[2] $Mn_{1.5}Mo_8O_{11}$,[3] $ZnMo_8O_{10}$,[4] $Ho_4Mo_4O_{11}$,[5] and $Gd_4Mo_{18}O_{32}$.[6] $Fe_{1.89}Mo_{4.11}O_7$ belongs to the $M_2Mo_4O_7$ family and represents a sixth structure type.

Because this $M_2Mo_4O_7$ member has distortions and cation nonstoichiometry, as represented by the formulation $(Fe_{1.89}Mo_{0.11})Mo_4O_7$, a superstructural ordering seemed likely. $Fe_{1.89}Mo_{4.11}O_7$ can be easily prepared in high yields, and thus, was considered a good candidate for the study of such long-range order. However, the crystals used for the x-ray diffraction studies were rather small, and thus, supercell reflections were quite weak. The search for long-range ordering was unsuccessful by conventional diffractometer methods. With the information derived from the subcell structure, complemented by microprobe analyses and Mössbauer spectroscopy, electron diffraction via transmission electron microscopy (TEM) was utilized for further study of this phase.

II. EXPERIMENTAL

$Fe_{1.89}Mo_{4.11}O_7$ was prepared as single phase material from stoichiometric quantities of Fe_2O_3 (J.T. Baker, "Baker Analyzed", 99.2%), MoO_3 (Fisher, Certified A.C.S.), and Mo metal (Aldrich, 99.9+%). Prior to the reaction, the thoroughly mixed reagents were loaded into a Mo tube (Thermo Electron, 99.993%) and evacuated to $\sim 2 \times 10^{-5}$ Torr before sealing via

electron beam welding. The Mo tube was protected by an argon atmosphere while the reaction was fired at 1300 °C for three days. The reaction was cooled at ~100 °C/h to 500 °C and then furnace cooled to room temperature overnight. The product found in the Mo tube was a black, highly crystalline powder. Powder x-ray diffraction, using an Enraf Nonius Delft FR552 triple focusing Guinier camera employing Cu K_{α_1} radiation (λ = 1.540562 Å), indicated that the material was single phase, based upon the parameters previously determined by single crystal indexing.[7] National Bureau of Standards silicon powder was used as an external standard.

A Philips CM30 transmission electron microscope was used to investigate the presence of superstructural ordering. An approximate one to one mixture of microcrystalline sample and G-1 Epoxy from Gatan was placed between lens paper, pressed between aluminum plates, and cured at 120 °C for 10 min. A 3 mm disk was punched out, thinned to ~20 μm by dimpling, put on a 200 mesh copper grid for support, and subsequently ion milled until a hole was observed. The sample and supporting grid assembly were then loaded into the TEM sample holder for investigation. All studies were completed at 300 keV.

III. RESULTS

The selected area diffraction (SAD) patterns for the [100], [010], [001], [110], [101], and [011] subcell zone axes were collected for $Fe_{1.89}Mo_{4.11}O_7$. All the strong reflections could be indexed based upon the d-spacings derived from the single crystal lattice parameters [*Imma*, no. 74, a = 5.9793(5) Å, b = 5.7704(4) Å, and c = 17.036(1) Å].[7] Any other reflections observed were presumed to be the result of superstructural ordering. The supercell reflections are labelled with a subscripted "sup", and all other reflections and zone axes are with reference to the subcell. All the presented SAD patterns also have accompanying computer-generated patterns which were based upon the derived supercell. The SAD's of the [100] and [110] zone axes, as shown in Figs. 1 and 2, can be fully indexed based on the known body-centered ($h + k + l = 2n$) orthorhombic symmetry and showed no superstructural information. Between pairs of subcell reflections in the [001] SAD of Fig. 3 [i.e., (000) and $(200)_{sub}$], a very weak pair of reflections is observed and corresponds to $\{2k0\}_{sup}$ and $\{4k0\}_{sup}$. The strongest superlattice reflections appear in the region between (000) and $(hk0)_{sub}$, and could also be indexed as $\{2k0\}_{sup}$ and $\{4k0\}_{sup}$. This information can be interpreted as a tripling in the a direction. These supercell reflections deviate from the body-centering condition ($h + k + l = 2n$). Note the slight streaking in these superlattice reflections; this observation would imply that the ordering in the a direction is not completely well-behaved; i.e., it has a short-range order, or there are distortions related to the framework along a^*. Close examination of the [101] zone axis, shown in Fig. 4, reveals that two maxima exist within the supercell streaking and can be indexed as $\{h2h\}_{sup}$ and $\{h4h\}_{sup}$. These supercell reflections indicate a tripling in the b axis, however, only with short-range order,

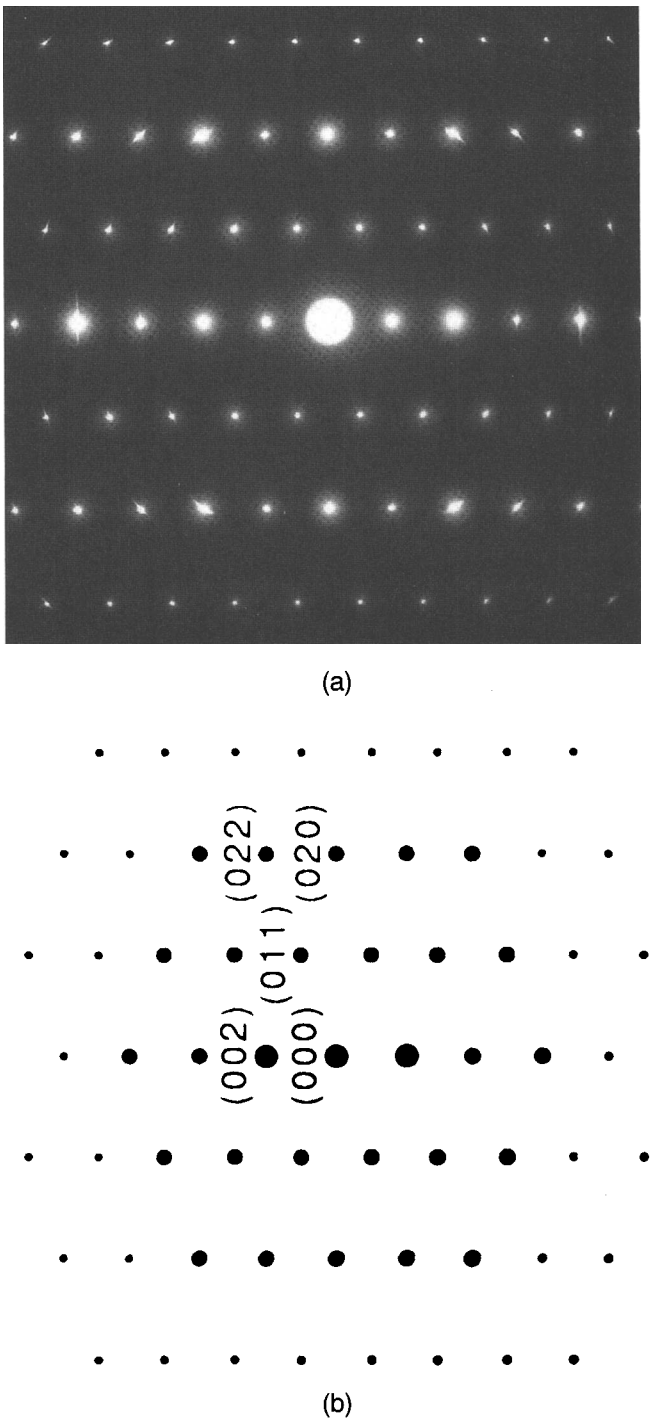


FIG. 1. (a) Selected area diffraction pattern for the [100] and (b) the computer-generated pattern for $Fe_{1.89}Mo_{4.11}O_7$.

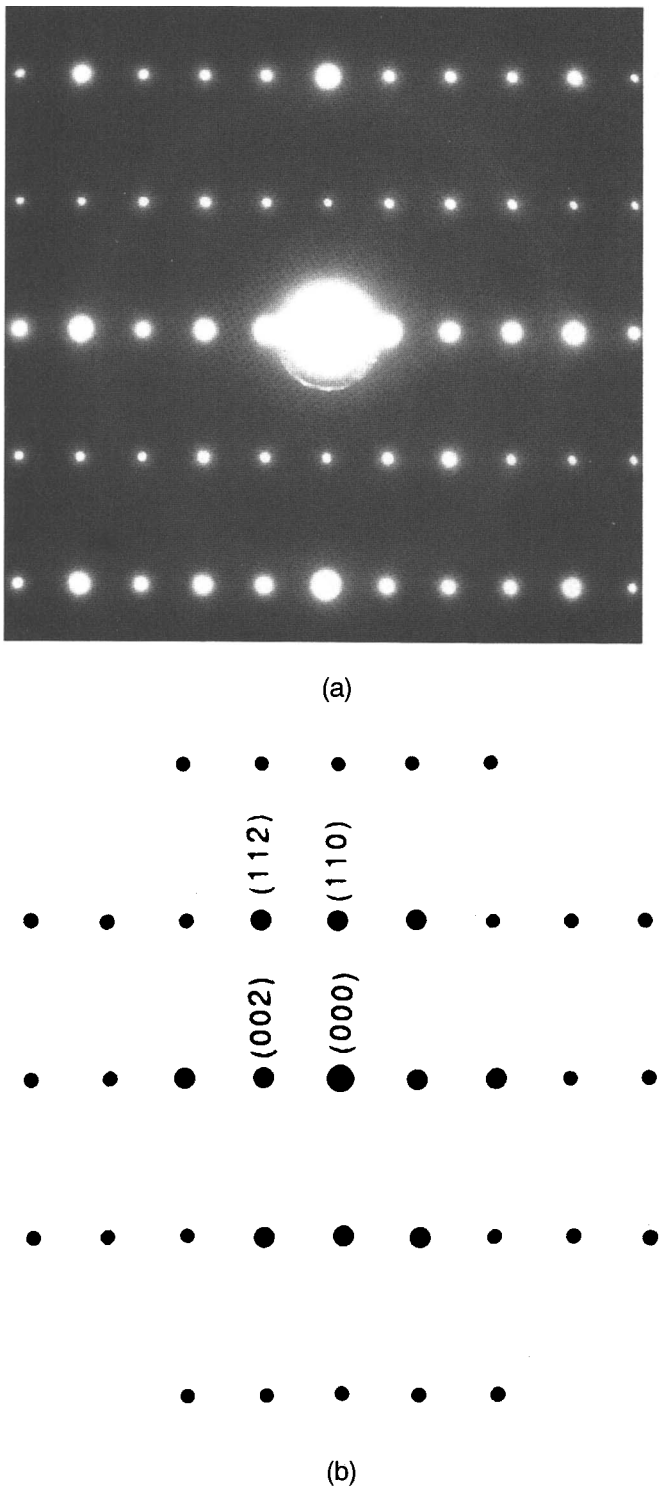


FIG. 2. (a) Selected area diffraction pattern for the [110] and (b) the computer-generated pattern for $Fe_{1.89}Mo_{4.11}O_7$.

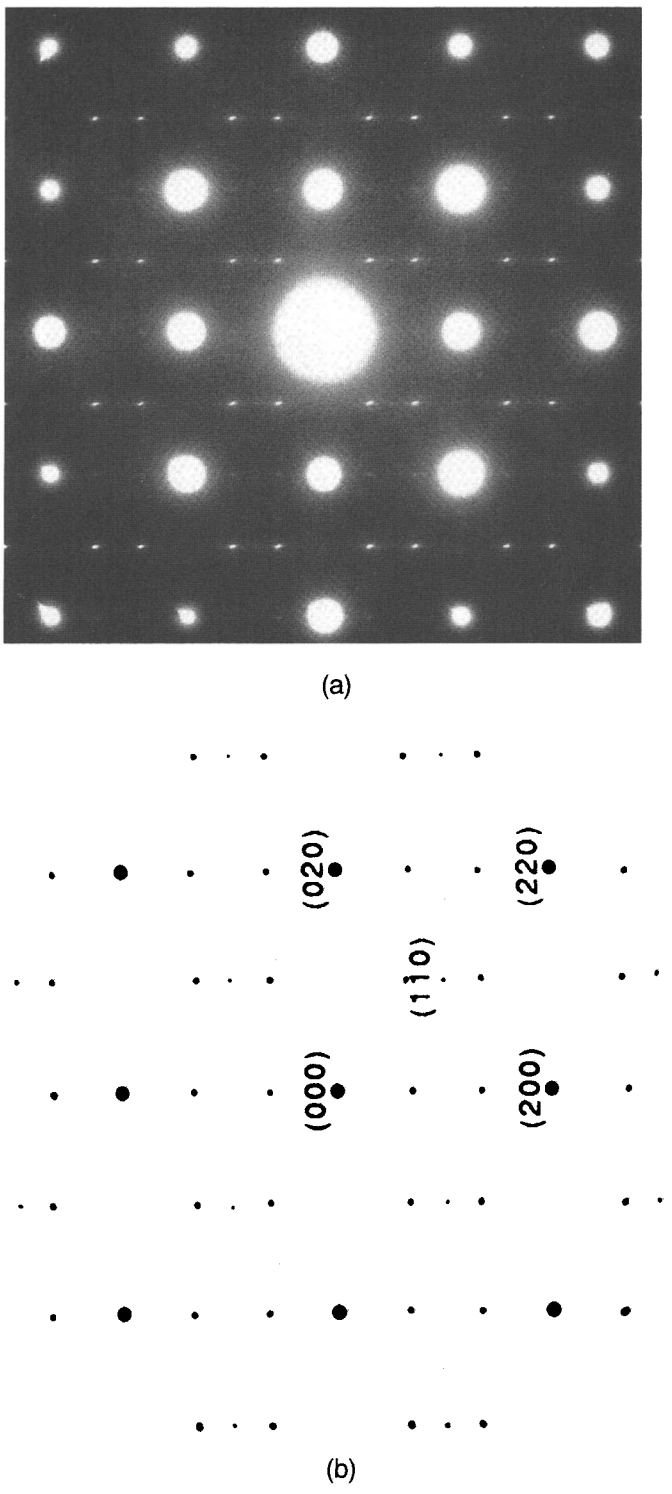
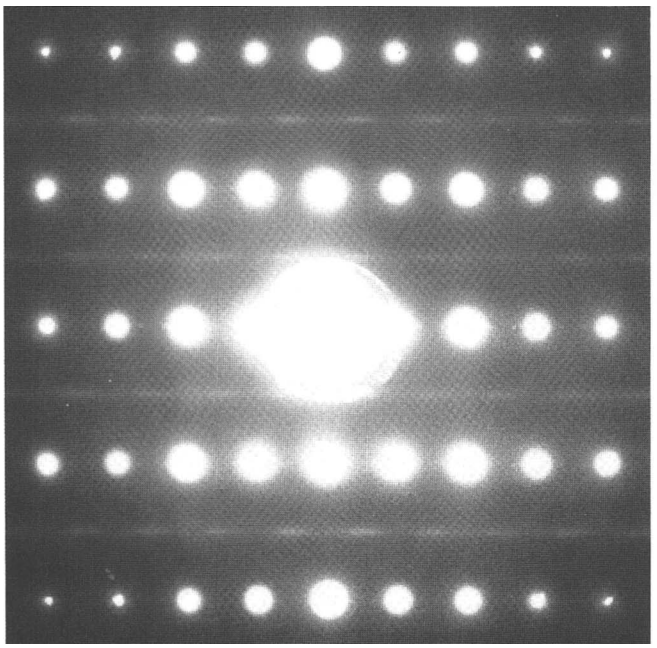
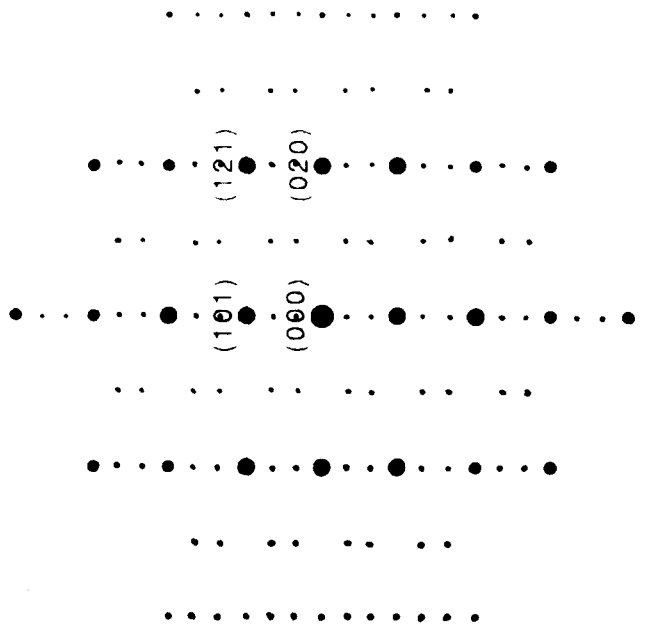


FIG. 3. (a) Selected area diffraction pattern, and (b) the computer-generated pattern for the [001] of $Fe_{1.89}Mo_{4.11}O_7$.

based upon the streaking. The same class, $\{h2h\}_{sup}$ and $\{h4h\}_{sup}$, can also be faintly observed between strong subcell reflections in the [101]. The [011] zone axis displays a superlattice reflection on either side of each subcell reflection, as exhibited in Fig. 5. These d-spacings correspond to the $\{1kl\}_{sup}$ and $\{5kl\}_{sup}$ and a tripling in the a direction; again, significant streaking is visible. Figure 6 displays the SAD of the [010] zone axis. In broad perspective, the superlattice diffraction in this zone axis appears as a pair of reflections above

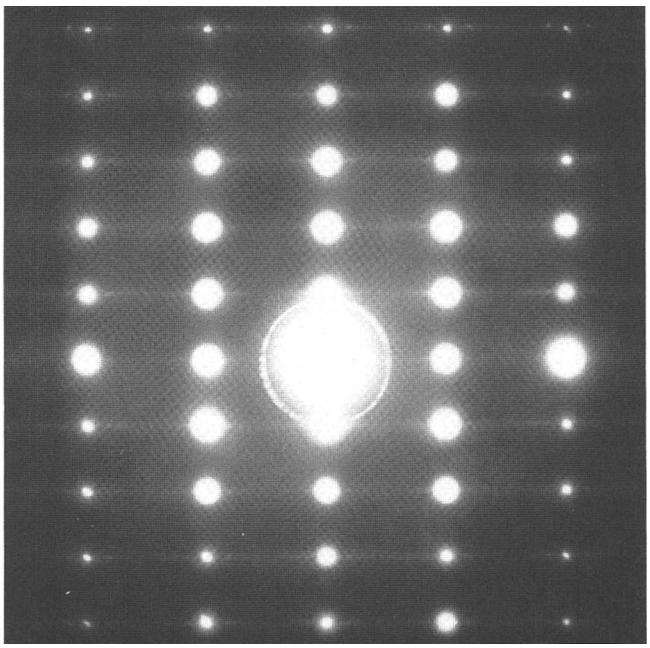


(a)

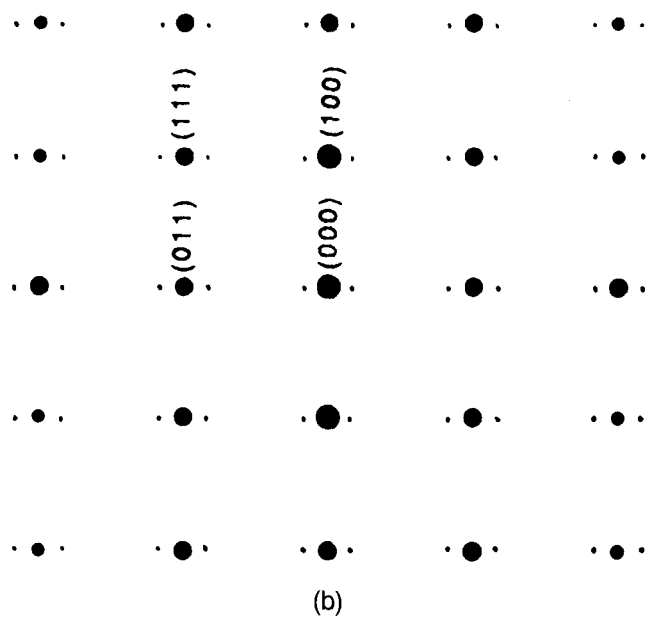


(b)

FIG. 4. (a) Selected area diffraction pattern for the [101] and (b) the computer-generated pattern for $Fe_{1.89}Mo_{4.11}O_7$.



(a)



(b)

FIG. 5. (a) Selected area diffraction pattern for the [011] and (b) the computer-generated pattern for $Fe_{1.89}Mo_{4.11}O_7$. Streaking has been omitted in (b).

and below every subcell reflection. Based upon the interplanar spacings, the supercell diffraction ($\{h0l\}_{sup}$, $h + l = 2n$) reflects a tripling in the a and c axes. All the observed reflections in the [010] also conform to the body-centering condition ($h + k + l = 2n$), although some reflections that fit this condition, such as the $(200)_{sup}$, appear to be too weak to be observed.

IV. DISCUSSION

The SAD information reveals an ordered superstructure in which all three lattice dimensions are tripled: $a' \sim 17.9$ Å, $b' \sim 17.3$ Å, and $c' \sim 51.1$ Å. The molybdenum-oxide framework might still be body-centered; however, the violations of this condition in the supercell indicate that the long-range order of the cations results in a primitive supercell. The streaking observed

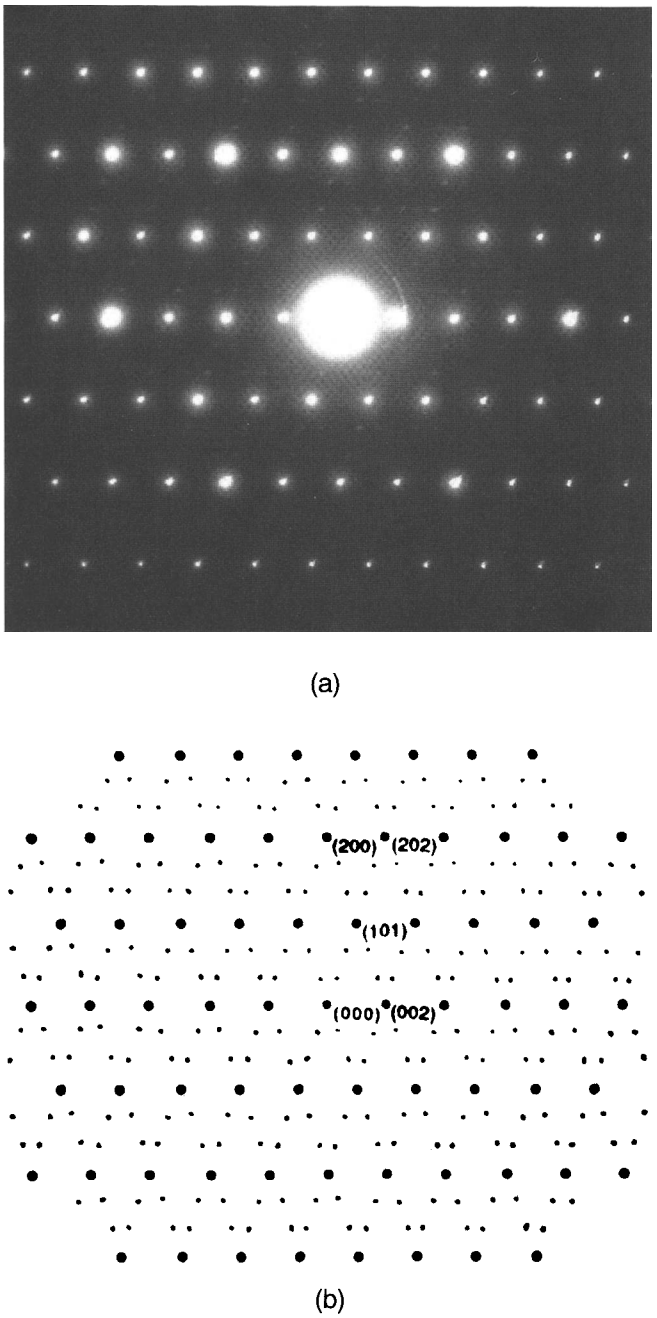


FIG. 6. (a) Selected area diffraction pattern for the [010] and (b) the computer-generated pattern for $Fe_{1.89}Mo_{4.11}O_7$.

in the diffraction patterns was variable from crystal to crystal; therefore, this $M_2Mo_4O_7$ phase has various degrees of ordering. When the superstructural ordering was well-behaved, one model, a $3 \times 3 \times 3$ supercell, accounted for the observed diffraction patterns.

The $Fe_{1.89}Mo_{4.11}O_7$ phase can be described as a close-packing of molybdenum-oxide cluster chains, $[Mo_4O_7]_\infty^{X-}$, in such a manner that tetrahedral and octahedral coordination sites are created. The cations reside in these two coordination environments. Analogous compounds in this series have been characterized, in which the octahedral sites are filled by a combination of cations, including Fe, Zn, Sc, Ti, Al, and/or Mo. Tetrahedral sites in these materials have been filled by only two cations, Fe or Zn.[8] Specific structural subcell details and properties of the $M_2Mo_4O_7$ phases will be published elsewhere.[7]

The $Fe_{1.89}Mo_{4.11}O_7$ subcell structure, as viewed in the ORTEP[9] (70% thermal ellipsoids) of Fig. 7, can also be described in terms of layers. The first layer contains infinite chains of trans edge-shared molybdenum octahedra, bridged on their edges by oxygen atoms. The chains then are interconnected via oxygens that bridge the basal plane edges of the Mo octahedra. These oxygen atoms, O1, are centered between four molybdenum atoms and are essentially coordinated in square planar geometry. The next layer contains metal-centered oxygen octahedra that share trans edges and run orthogonal to the infinite metal-metal bonded Mo chains. These octahedral sites, M2, are occupied by 89% Fe and 11% Mo. The layers are then repeated by using the body-centering operation. Also, iron atoms, Fe1, fill sites tetrahedrally coordinated by oxygen between each of the orthogonal layers.

As can be seen from Fig. 7, the *a* axis, ~6.0 Å, runs from the center of the lower left Mo octahedron to the center of the lower right Mo octahedron. The *b* axis is parallel to the viewing direction and is two edge-sharing molybdenum octahedra deep. This repeat distance, ~5.8 Å, is necessary due to the placement of tetrahedral and octahedral sites along *b* and the distortion in the apical-apical Mo–Mo bond distances, creating an alternating short-long arrangement. The *c* axis extends vertically approximately 17 Å from the center of one molybdenum octahedron to the center of the molybdenum octahedron directly above it.

One underlying presumption in the model to be discussed is that the iron and molybdenum atoms, which are mixed on the octahedral sites (M2) of the subcell, are the root of the superstructure that is observed. Within each subcell there are two "chains" of MO_6 units, as denoted by arrows in Fig. 7, and each chain has two M2 atoms per unit cell. Therefore, a tripling in the lattice parameters will generate six layers of octahedral sites, each layer containing $(2 \times 3 \times 3)$ or 18 M2 atoms. Two molybdenum and 16 iron atoms (11% and 89%) will result in a nearly identical composition that was refined by the single crystal study [$Fe_{1.84(2)}Mo_{4.16(2)}O_7$ or Fe/Mo = 0.44][7] and verified by microprobe analyses (Fe/Mo = 0.46).[8(c)] For discussion purposes, a body-centered symmetry operation will be used, with the realization that this symmetry constraint is easily violated by interchanging a single Mo and Fe atom. The consequence of this rearrangement would be an even larger supercell, although such a situation would prove difficult to observe even by TEM. However, the observed SAD streaking

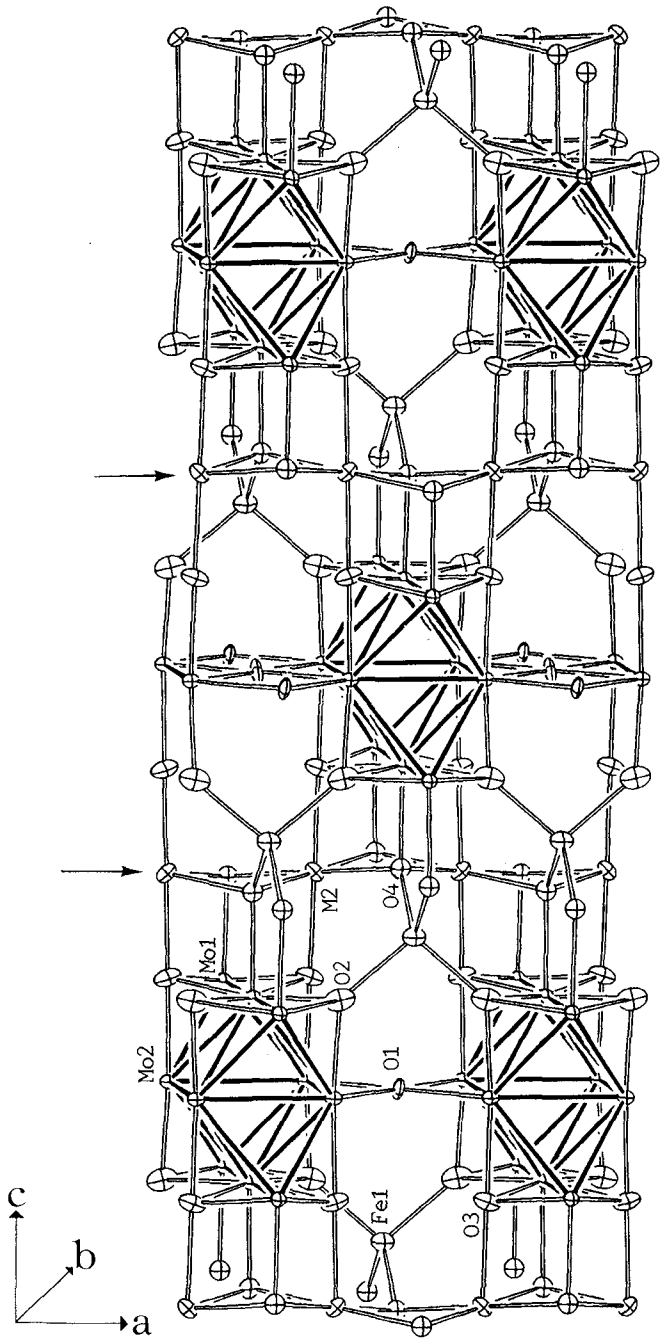


FIG. 7. The unit cell, as viewed parallel to the b^* axis, of $Fe_{1.89}Mo_{4.11}O_7$. Dark bonds denote metal-metal bonding and open lines denote metal-oxygen bonding. Arrows indicate unit cell axes and MO_6 layers.

might be the result of the loss of body-centering and short-range order. Finally, Mössbauer experiments on $Fe_{1.89}Mo_{4.11}O_7$ at room temperature showed that three different kinds of iron existed in this compound. One kind corresponds to iron in the tetrahedral sites. The other two, in relative abundance 3 : 1, occupy the octahedral sites. Thus, there are three iron atoms (M2) with iron neighbors (M2) (to be represented 3 Fe/Fe) for every Fe (M2) atom with a neighboring Mo (M2) atom (to be represented 1 Fe/Mo).[7] Based upon the conditions given, representations of the supercell octahedral layers are shown in Fig. 8. Layers 1 and 4, 2 and 5, and 3 and 6 are related to each other by the body-centering operation. Note that in all cases the *2mm* symmetry is preserved. Layers 1 and 4 conform to the Mössbauer requirements with 12 Fe/Fe to 4 Fe/Mo. Layers 2 and 5 have 6 Fe/Fe to 8 Fe/Mo; these values are half the ratio shown by Mössbauer; however, if layers 3 and 6 are all iron (18 Fe/Fe to 0 Fe/Mo), then layers 2, 3, 5, and 6 average to 3 Fe/Fe to 1 Fe/Mo. This superstructure results in an average ordering of 1 molybdenum atom over 9 octahedral cation sites and, therefore, generates the fol-

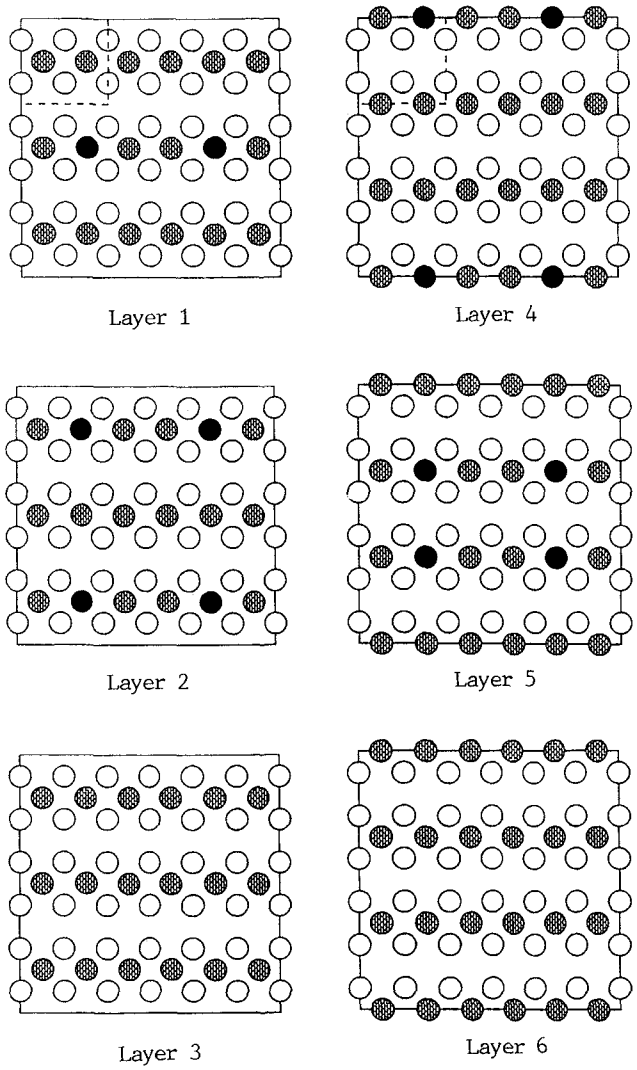


FIG. 8. The layers of MO_6, indicating the Mo/Fe ordering in a superstructure of $Fe_{1.89}Mo_{4.11}O_7$. (○) oxygen atoms, (●) molybdenum atoms, and (◍) iron atoms. The dashed lines indicate the subcell *a* and *b* axes.

lowing empirical formulation: $(Fe_8Mo_1)^oFe_9^tMo_{36}O_{63}$, where t and o represent tetrahedral and octahedral ternary metal sites, respectively. Based on the multitude of crystals examined, $Fe_{1.89}Mo_{4.11}O_7$ either has an ordered superstructure as described above, or short-range order existed, as indicated by SAD streaking.

V. CONCLUSIONS

$Fe_{1.89}Mo_{4.11}O_7$ contains an ordered superstructure, which was derived from SAD patterns via TEM. The long-range order can be described by a $3 \times 3 \times 3$ supercell. The subcell is constructed from a close-packing of the Mo–Mo bonded octahedra, resulting in the formation of tetrahedral (Fe) and octahedral (Fe and Mo) cation sites. The superstructural arrangement has been represented as an ordering of layers of those iron and molybdenum atoms which reside on sites having nearly octahedral coordination by oxygen.

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